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A METAL-CONNECTED GLASS ELECTRODE

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ABSTRACT

Glass electrodes have come into extensive use for the measurement of hydrogen-ion activity in special cases in which other kinds of electrodes are unsuitable. Previous methods of construction have produced glass electrodes which were fragile, had an uncertain length of life, and required connecting in circuit with two standard electrodes.

In the work reported in this paper a glass electrode was developed which has a comparatively thick wall and a direct metallic connection to the glass. This makes a very durable apparatus and eliminates one standard electrode from the circuit. It is shown that the accuracy of such a metal-connected glass electrode is comparable with that of other electrodes used in pH measurement.

CONTENTS

	Page
I. Introduction	833
II. Historical	834
III. The metal-connected glass electrode	835
1. Principle	835
2. Construction	836
IV. Experimental work and conclusions	839
1. Apparatus and general methods	839
2. Useful pH range	845
3. Effect of age	845
4. Effect of alkali salts (salt error)	846
5. Effect of heavy metal salts	848
6. Effect of protein	850
7. Effect of oxidants and reductants	850
8. Applications	851
V. Summary	852
VI. Acknowledgments	852
VII. Bibliography	852

I. INTRODUCTION

The glass "electrode," or, more strictly speaking, the glass half-cell, has come into extensive use recently to measure hydrogen-ion concentration in certain kinds of solutions for which other types of electrodes are unsuitable. Its advantages include freedom from disturbance by oxidation-reduction potentials and obviation of added reagents, such as gaseous hydrogen or solid quinhydrone. Its disadvantages are the inherent high resistance (at present greater than 1 megohm), requiring the use of delicate or special apparatus for detecting potential changes; and the fragility, which makes the useful life short or uncertain. The purpose of this investigation was to remove or reduce these disadvantages.

II. HISTORICAL

The discovery of a reaction between glass and hydrogen ions goes back at least to Cremer (1).[1] Haber and Klemensiewicz (5), who acknowledged Cremer's work, appear to have been the first to actually apply the principle to laboratory measurements. Their systematic and extensive treatise is so well known that they are usually credited with the development of the glass electrode in something like its present form. As often happens, over a decade elapsed before further notice appeared, and about 20 years passed before general interest in the subject was aroused.

Numerous theories have been proposed to account for this peculiar action of glass. These theories may be roughly classified into three groups, based on phase boundary, ion adsorption (or exchange), and liquid junction (or diffusion) potentials. All of these seem to imply that the glass contains or attracts water and hydrogen ions (protons), and some of them imply that only hydrogen ions can penetrate into or through the glass. The situation is complicated by the fact that glass is not unique in this respect. Thus, similar effects have been detected at interfaces of water with quartz (41), paraffin, zeolite minerals (19, p. 252), and benzene (5). Borelius (8, p. 447) summarize concisely three possible conditions for electrode action. Much information on the theoretical aspects will be found in recent papers by MacInnes and Belcher (34), and by Dole (35) (44).

The composition of the glass used is important and has been studied by Hughes (23), MacInnes and Dole (27) (31), Elder (29), and others. Most investigators agree that a soft glass containing about 22 per cent of Na_2O, 6 per cent of CaO, and 72 per cent of SiO_2 [2] gives the best results. Means to effect further improvement in the electrode action of glass are not now apparent, but it is conceivable that the abnormalities shown in very acid and alkaline solutions might be decreased by the addition of other substances to the glass.

Small bulbs with thin walls have been used by most investigators, including Haber and Klemensiewicz (5), Hughes (9) (23), Elder and Wright (25), Voegtlin, De Eds and Kahler (32), Robertson (36), and others. Kerridge (20) modified this construction by blowing a local reentrant thin area (0.025 to 0.030 mm thick) in the bulb wall to serve as the active surface. Horovitz (15, p. 345) sealed a relatively thick (0.05 to 0.1 mm) plate of glass on the end of a glass tube. MacInnes and Dole (27) used an electrode of similar shape, but with an extremely thin (0.001 mm) active surface, about 4 mm in diameter, obtained from the wall of a glass bubble. This might be called a "membrane" electrode. The forms described may be conveniently classified into the two general types of bulb and membrane, although there appears to be no essential difference in their action. Figure 1 shows several types of electrodes and methods of connection.

The characteristic arrangement for these active glass surfaces has been with a solution on each side of the bulb or membrane wall. One solution is of known or fixed hydrogen ion activity, while the other is of unknown or variable activity. This in effect makes a hydrogen

[1] Figures in parenthesis here and throughout the text refer to the numbers used in the bibliography at the end of this paper.

[2] Commercial glass of this composition is obtainable, for instance, No. 015 glass of the Corning Glass Co., Corning, N. Y. Tubing with an outside diameter of 7 mm, and 1 mm wall is convenient for blowing membrane electrodes.

electrode on each side of the glass. A standard electrode of some sort is immersed in each solution to complete the circuit. These standard electrodes need not be identical but, if so, their potentials are opposed and cancel each other in the measurement. It is important to note that in this arrangement only electrolytic contact is made with the glass.

Maximum sensitivity is associated with minimum resistance, and consequently the tendency has been to make the glass as thin as possible. For small electrodes, the practical lower limit of resistance thus reached lies between 2 and 50 megohms (27) (34) (36), as determined by direct-current measurement (27) (34). The best electrodes thus become rather difficult to construct, excessively fragile, and of uncertain life even with careful handling.

Where extreme compactness is not required, more durable, although not necessarily as sensitive, electrodes of the same resistance could obviously be prepared by using a thicker wall with a larger area. The bulb type is better suited to this modification than the membrane type, as it is difficult to properly seal a large area of membrane. Hazel and Sorum (39), however, have recently increased the membrane diameter to about 10 mm. On the other hand, the results obtained by Robertson (36) indicate that it is possible to form a comparatively small bulb having a resistance as low as that of a membrane.

The situation described limits the widespread use of glass electrodes, especially in industrial work, where rugged and permanent apparatus is desirable.

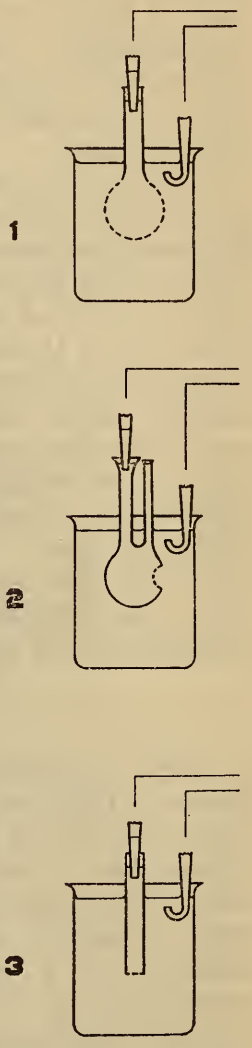

FIGURE 1.—*Forms of the ordinary glass electrode*

(The active surface portion is shown in dotted line. Each glass electrode is connected to two calomel electrodes, of which only the tips are shown.) 1, plain bulb; 2, reentrant bulb; 3, membrane

III. THE METAL-CONNECTED GLASS ELECTRODE

1. PRINCIPLE

In connection with the mechanical advantages of thick-walled electrodes, it appeared possible to greatly simplify the mounting and eliminate the extra (inside) standard electrode by substituting a direct metallic connection to the glass wall. With glass of sufficient thickness to withstand ordinary handling, for instance, 0.1 to 0.5 mm, such a metallic connection could be easily applied and would furnish additional protection to the glass. This was tried (March 25, 1930) by wrapping tinfoil around a soft-glass tube, and the results were promising enough to warrant further trial and development, as reported in this paper.

No publication has been noted which describes the use of a metal to glass connection for the systematic accurate measurement of hydrogen-ion concentration. Previous investigators have doubtless made incidental trials of a simple metallic connection, such as mercury within a glass bulb, analogous to the mercury cups so often used in

making electrical contact with sealed-in wires on glass apparatus. B. von Lengyel (41, pp. 426 and 431) tried a mercury to quartz connection, but found it to be unsatisfactory. He also used a Wood's metal to quartz connection for checking an electrode chain. Haber and Klemensiewicz (5, p. 424) used a connection, not with glass, but with a layer of benzene, by means of an immersed disk of amalgamated brass. Many experiments have also been published describing electrolysis through glass, or determinations of the conductivity of glass, in which electrodes of metal, amalgam, or powdered graphite were applied.

The exact function of the metal coating on a "metal-connected" glass electrode has not yet been determined. If, as is very generally believed, conduction through glass is entirely electrolytic; that is, due to the movement of ions, there may be set up a metal-metal oxide or metal-metal silicate electrode with a comparatively steady potential. If the passage of current through the glass results from electronic—that is, solid conduction—the metal serves, of course, merely as a convenient terminal. Besides being a conductor (or nonconductor according to the point of view) glass is also a dielectric; that is, it transfers charges by induction. The apparatus used for detecting a change of potential in the circuit is capable of measuring static charges. This point will be mentioned subsequently in connection with the details of construction. It should be emphasized, however, that further work will be required to furnish a satisfactory explanation of the complicated phenomena involved.

2. CONSTRUCTION

There are obviously many ways of arranging a metal-glass electrode. Thus, wires, rods, sheets, and tubes of suitable metals might be coated with a film of the proper glass; or, conversely, tubes, beakers, flasks, and other vessels of the proper glass might be coated with a film of an appropriate metal. The latter might be applied by pressure, spraying, casting, sputtering, or chemical precipitation from a solution or a gas, and subsequently thickened and protected by electroplating. Various possible arrangements are shown in Figure 2.

The metal-connected glass electrodes first employed in this investigation were constructed from various stocks of laboratory tubing, using tinfoil on those containing the solution to be tested, and mercury or coiled wire inside those dipping into the solution. Subsequent work showed that glass having the composition ordinarily used for membranes also gave the best results for metal-connected electrodes, and that silvering followed by copper plating gave a more durable and satisfactory coating than tinfoil. Electrodes of the dipping type were found to be less accurate than those of the containing type. Further investigation is needed, but this difference may be the result of greater dehydration of the outer surface during the working of the hot glass.

For the final exploratory work, three containing and three dipping type electrodes were prepared from Corning No. 015 glass tubing by blowing it into the shape of test tubes with walls about 0.5 mm thick. These tubes had an outside diameter of 1.2 cm and a length of 12 cm, and contained (or displaced) about 10 ml of solution. Silvering was applied on either the inside or outside surface by the Rochelle salts

process (37), and copper [3] was then deposited to a thickness of about 0.008 mm. The glass tubes were coated with paraffin for about 1 cm on the outside at the open end to diminish surface leakage. A copper

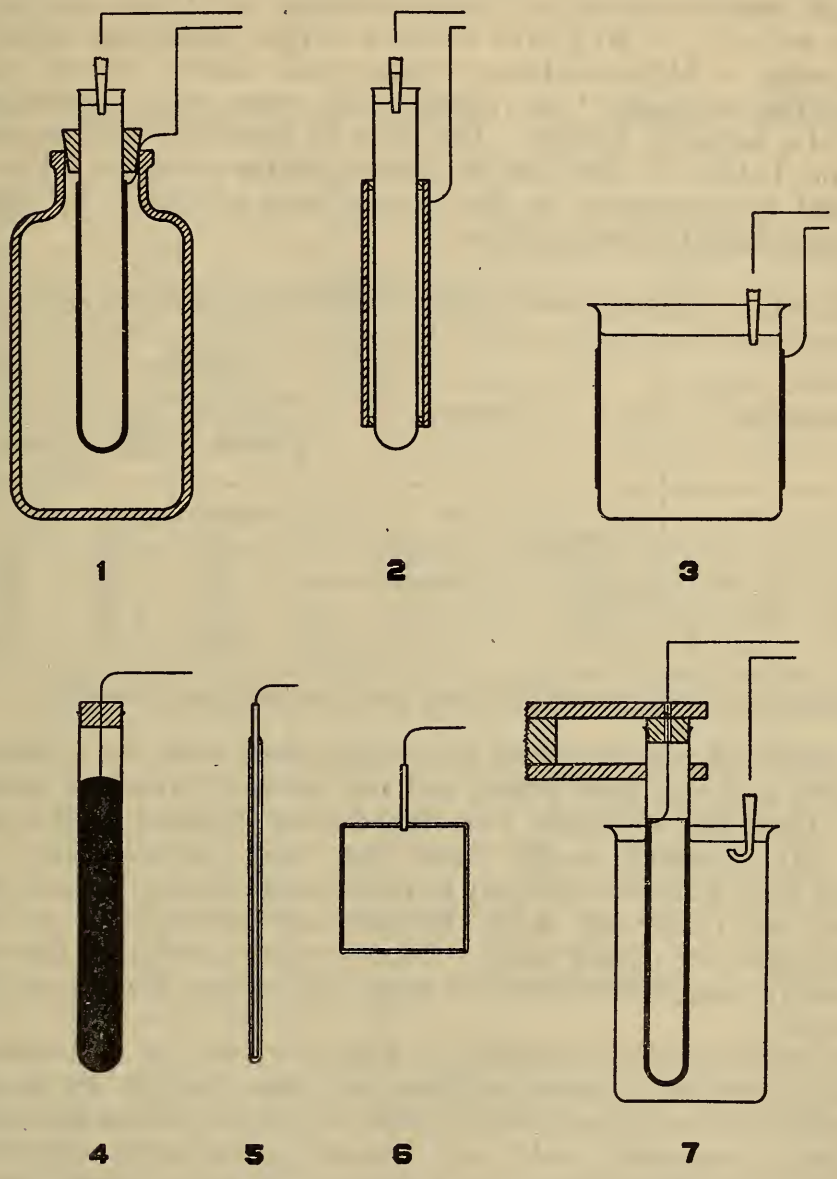

FIGURE 2.—*Arrangements of the metal-connected glass electrode*

(Only the tips of calomel electrodes are shown.) 1, Containing type; tube form, metal coated; 2, containing type; tube form, with metal portion insulated from the glass by means of mica wedges at top and bottom, and an air gap. For special study; 3, containing type; beaker form, metal coated; 4, dipping type; tube form, mercury filled; 5, dipping type; metal rod or wire form, coated with glass; 6, dipping type; metal sheet form, coated with glass; 7, dipping type; tube form, metal coated and supported by bakelite clamp.

wire was wrapped or pressed against the metal coating and the completed electrode was mounted in a suitable support. This consisted

[3] Plating on the outside was done with a solution containing 100 g/l of $CuSO_4.5H_2O$. The coating was applied by "flashing" at a current density of about 5.5 amp/dm² for a few minutes, after which plating was continued at 0.6 amp/dm² for one-half hour. Plating on the inside was found difficult on account of the small bore and consequent poor circulation. Satisfactory results were finally obtained by using a more concentrated solution containing 250 g/l of $CuSO_4.5H_2O$, and an accurately centered copper wire as anode. Because of the necessarily excessive anode current density, the 110-volt circuit with a rheostat in series was required to overcome anode polarization. A flash of copper was applied at about 5 amp/dm² for one minute, after which plating was continued for one and one-half hours at 0.36 amp/dm². All plating was done at room temperature. The copper coating was lacquered, except at the pressure contact with the connecting wire

of a rubber-stoppered glass bottle for a containing electrode and a bakelite clamp on a stand for a dipping electrode. (See fig. 2, Nos. 1 and 7.)

Rough measurements of the resistance of these electrodes, in contact with 0.1 *N* HCl into which a copper wire was dipped, were made using a high-resistance bridge and direct current at 1,000 volts.[4] The capacity [5] at 1,000 cycles was also determined, by means of a capacity bridge. The data on resistance and capacity are given in Table 1. Because of their greater accuracy, the results presented subsequently in this paper were obtained by means of electrodes of the containing type.

TABLE 1.—*Resistance and capacity of metal-connected glass electrodes*

Electrode No.	Type	Resistance		Capacity	
		Initial	After 8 months	Initial	After 8 months
		megohm	*megohm*	*μμf*	*μμf*
1 [1]	Containing	43	53	590	625
2	do	37	39	660	695
3	do	48	55	535	555
4	Dipping	57	58	460	505
5	do	53	48	530	525
6	do	53	60	510	495

[1] The resistance of this electrode when previously coated with tinfoil was 70 megohms.

In actual use, the electrode was rinsed once with the solution to be measured and was then filled, and the potential reading obtained at once. Then the electrode was rinsed with distilled water and kept filled with distilled water until the next measurement. When working with solutions difficult to remove by rinsing, it was necessary to clean the electrodes with chromic acid solution, or to immerse them in water for a long time. Recovery from ordinary disturbances was usually complete within one hour and almost always on standing over night.

The special electrode shown in Figure 2, No. 2, was constructed with the metal side insulated from the glass, mainly by an air gap. The resistance was thus raised to 5,000 megohms, with a corresponding reduction in capacity to 45 *μμf*. Readings on buffer solutions were unsteady, but an accuracy of about ±0.5 pH was obtained even under these very unpromising conditions. This experiment indicated that electrode action does not require actual contact between

[4] This scheme was used merely for convenience and is not suggested for general use. The application of a high voltage tends to cause the passage of appreciable current, with the possibility of polarization and disturbance to readings. These electrodes were affected temporarily, as shown at *A* in Figure 7; but after standing in contact with water for a few weeks, they returned to the original condition.

It has been pointed out by MacInnes and Belcher (34) that resistance measurements on glass electrodes made with direct current are conventional and that alternating current gives much lower and more accurate results. They concluded, however, that: "It does not appear desirable to change the current practice of reporting the apparent direct-current resistances of electrodes in megohms."

In measurements using direct current, MacInnes and Dole (27), (31) applied much lower voltages, either 3.7 or 1.2 volts; MacInnes and Belcher (34) applied less than 1 volt. It may be pointed out that the surface ratio of a metal-connected electrode to a membrane electrode, each of the usual size, is about 3,300 to 12 mm². The application of 1,000 volts on the former produces the same current density as does 3.6 volts on the latter, if both have the same total resistance. As a matter of fact, the direct-current resistances obtained for the metal-connected glass electrodes are of the expected order of magnitude, when compared with the direct-current resistances of membrane electrodes as measured by the author, using the method of MacInnes and Dole (27) (31).

[5] Residual noise in the telephones indicated a wide phase angle. This is characteristic of low dielectric resistance, or of a "leaky" condenser.

metal and glass. Completion of the circuit may have been effected through surface leakage, or possibly by induction. In this connection, Borelius (6) (7) (8) has published many measurements including electrolytic potentials at glass or paraffin surfaces, where an air gap was used in the circuit.

IV. EXPERIMENTAL WORK AND CONCLUSIONS

1. APPARATUS AND GENERAL METHODS

Potential measurements were made with a "student type" potentiometer calibrated to ±0.5 mv. A Compton quadrant electrometer[6] was used as the indicating instrument in the glass electrode measurements, by the null-point method. The saturated potassium chloride-calomel reference electrode was employed. For standardization of buffer solutions and for comparative readings, other electrodes were used, including the hydrogen (with platinum black), the quinhydrone (with gold), and the glass membrane (with Corning No. 015 glass).

The glass-membrane electrodes were mounted or connected, not through an inside silver-silver chloride electrode as used by MacInnes and Dole (27) but through a saturated calomel electrode according to the system of Kerridge (20) and others. The electrode was filled with any suitable buffer solution, into which dipped the plugged tip of the calomel electrode. The plug consisted of agar jelly saturated with potassium chloride, and this device was used for its mechanical convenience. Such devices are, of course, possible sources of error by the introduction of an additional potential into the circuit. The error in this case appeared to be negligible within the limits of accuracy sought. An alternative procedure would involve the use of an extremely small bent tip, or else a ground-glass seal (20). The second or reference calomel electrode had a bent tip, according to the usual scheme. (See fig. 1, No. 3.) Silver-silver chloride electrodes are more compact, but somewhat less convenient to prepare and maintain than calomel electrodes.

A saturated calomel electrode, having a tip plugged with agar jelly saturated with potassium chloride, was also used for connection with the containing type of metal-connected glass electrodes. (See fig. 2, No. 1.)

Potential readings were made at room temperature, usually about 25° C. As the saturated calomel electrode was used for reference and most of the solutions were buffered, the accuracy of the measurements was about ±0.1 pH (±6 mv). This was sufficient for the exploratory purposes of this investigation. The readings, including those with the metal-connected glass electrode, were made, however, to the nearest 0.02 pH (±1 mv) and occasionally to 0.01 pH (±0.5 mv). The observations indicated that with closer control of temperature and a decreased wall thickness the accuracy with this electrode could probably be made equal to the above precision.

Switches in the circuit of the electrometer and glass electrode were made of paraffin blocks with mercury-filled copper cups as terminals.

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[6] Where portability is required, the Lindemann electrometer may be substituted. Numerous circuits have been published in which the delicate and relatively expensive electrometer was replaced by vacuum tubes. A recent paper by Compton and Haring (47) described a compensated thermionic electrometer which is stated to have possibilities for use with thick glass electrodes. Robertson (36) reported the use of a galvanometer of high sensitivity with electrodes of very low resistance.

Fused sulphur would probably have been better than paraffin, but it is less easy to handle. The electrometer leads were insulated with mica and were run in grounded brass pipes, although bakelite insulation was used in a few places for convenience. The electrometer switches were placed in a grounded copper gauze cabinet, one compartment of which also served to hold and partially shield the glass-calomel

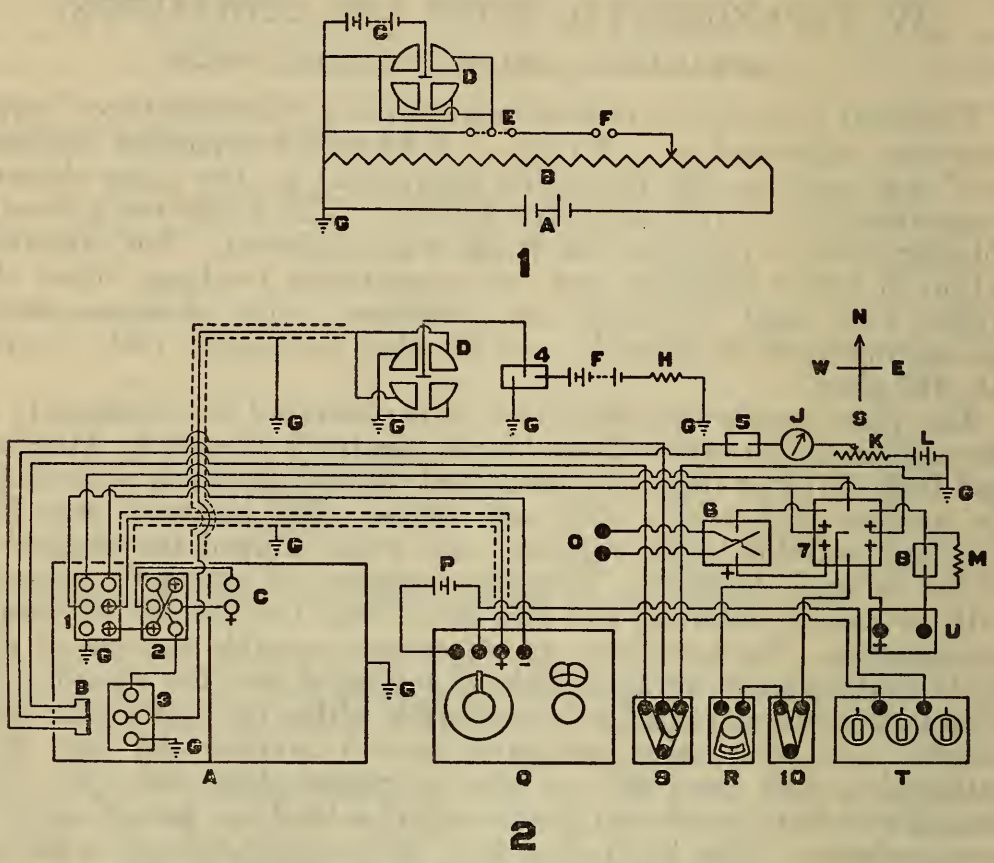

FIGURE 3.—*Wiring diagram of apparatus*

1. Simplified diagram for the potentiometer using an electrometer by the null-point method. *A*, Battery for potentiometer; *B*, potentiometer; *C*, battery for electrometer needle; *D*, electrometer; *E*, single pole double throw switch; *F*, binding posts for connecting glass electrode-standard electrode cell; *G*, ground. 2. Complete diagram (student type potentiometer). *A*, shielded cabinet holding special paraffin base switches and the glass electrode-standard electrode cell; *B*, electromagnets (1 ohm each) for tripping electrometer switch; *C*, terminals for connecting glass electrode-standard electrode cell; *D*, electrometer; *F*, battery for electrometer needle (it makes no difference which pole is connected to the needle); *G*, ground; *H*, protective resistance (0.1 megohm) for *F*; *J*, ammeter (1 ampere scale) for reading the electromagnet current; *K*, variable resistance (3 ohms) for controlling the electromagnet current; *L*, battery (3 volts) for supplying the electromagnet current; *M*, protective resistance (20,000 ohms) for standard cell; *O*, terminals for connecting hydrogen or quinhydrone electrodes; *P*, battery for potentiometer; *Q*, potentiometer (student type); *R*, galvanometer (desk type); *T*, variable resistance (1,000 ohms) for adjusting potentiometer; *U*, standard cell; *1*, paraffin base main D. P. D. T. switch; *2*, paraffin base reversing D. P. D. T. switch; *3*, paraffin base electrometer S. P. D. T. switch; *4*, porcelain base electrometer needle S. P. D. T. switch; *5*, porcelain base S. P. S. T. switch for *B* circuit; *6*, porcelain base D. P. D. T. reversing switch; *7*, porcelain base T. P. D. T. switch; *8*, porcelain base S. P. S. T. shorting switch; *9*, hard rubber base three point key; *10*, hard rubber base two point key. Switching directions, adjusting potentiometer, (*1*) north and (*7*) east. Set potentiometer by means of *U*, *R*, and (*10*). Using hydrogen or quinhydrone electrode, (*1*) north and (*7*) west. Hydrogen or quinhydrone electrode connected to *O* at north reads on potentiometer, using *R* and (*10*). (*6*) west for hydrogen electrode. (*6*) east for quinhydrone electrode and pH below 7.67. (*6*) west for quinhydrone electrode and pH above 7.67 (using saturated calomel electrode). Using glass electrode, (*1*) south, glass electrode reads on potentiometer, using the electrometer, close (*5*) to operate (*3*), use (*9*) for remote control of (*3*), set (*2*) as may be necessary.

cell. The main switch connecting the electrometer was tripped by an electromagnet operated by remote control from a key placed outside the cabinet. This device proved very convenient and eliminated any disturbance due to body capacity. The other paraffin switches needed only occasional shifting, which could be done manually without difficulty.

Electrometer disturbances could usually be traced to either too much or too little mercury, or to dirty mercury, in the switch cups. A quick, positive make or break is necessary and contact electromotive forces must be prevented. In view of occasional difficulties, however, the elimination of mercury is being considered, by means of a switch with solid contacts of the brush or spring type. It was preferable not to operate the electrometer at maximum sensitivity, on account of its instability. Best results were obtained with the particular instrument used by keeping the needle voltage as low as possible, about 70 volts usually being satisfactory. A scale deflection of 3 mm/mv at 1 m scale distance was then obtained by lift and tilt adjustment of the quadrants. This sensitivity was adequate for the present work, although a much higher sensitivity is possible and has been used at times by others (34).

It is occasionally stated that an electrometer can not be used in very humid weather. In these experiments, suitable measurements could be obtained up to 80 per cent humidity of the room atmosphere. This favorable result may have been due to special care in insulating and shielding the circuit. It was sometimes found advantageous to ground the glass electrode just before connecting it to the electrometer for a reading. This removed stray charges from the system.

The potentiometer circuit was so wired that either hydrogen, quinhydrone, or glass electrodes could be connected in the appropriate position and all necessary measurements could be obtained by means of permanently connected switches and keys. The wiring diagram is shown in Figure 3. When using a more accurate potentiometer, such as the "type K" which has more of the accessory apparatus located internally, certain changes would be required in the wiring (34, p. 3316). The equations applying to the respective electrodes when used at 25° C. in combination with a saturated calomel reference electrode are given in Table 2, in both an extended and a somewhat simplified form. The extended form shows the factors which control the first term on the right-hand side of the simplified equation used in the actual measurements. E is the measured cell potential, expressed in volts, from which the desired pH value is computed.

TABLE 2.—*Electrode equations at 25° C.*

Electrode	Extended equation	Simplified equation
Hydrogen (24, p. 672)	$pH=\frac{-E-0.2458}{0.05912}$	$pH=-4.16-\frac{E}{0.05912}$
Quinhydrone (24, p. 672)	$pH=\frac{0.6992-E-0.2458}{0.5912}$	$pH=7.67-\frac{E}{0.05912}$
Glass (*a*), mounted with silver-silver chloride electrode and 0.1 *N* HCl (28).	$pH=\frac{0.3524-E-0.2458}{0.05912}$	$pH=1.80-\frac{E}{0.05912}$
Glass (*b*), mounted with saturated calomel electrode and 0.1 *N* HCl (24, p. 672).	$pH=\frac{-E+0.0636}{0.05912}$	$pH=1.08-\frac{E}{0.05912}$
Glass (*c*), mounted with saturated calomel electrode and 0.05 *M* acid potassium phthalate (20).	$pH=\frac{-E+0.2349}{0.05912}$	$pH=3.97-\frac{E}{0.05912}$
Glass (*d*), mounted with saturated calomel electrode and any buffer solution of pH=*K*.	$pH=\frac{-E-E_K}{0.05912}$	$pH=K-\frac{E}{0.05912}$
Glass (*e*), metal-connected; *X* (determined by calibration) is the pH of the solution for which *E*=0.		$pH=X-\frac{E}{0.05912}$

In the equations of Table 2, liquid junction potentials and uncertainties in pH values have been disregarded, but in most cases these are too small to need consideration for the present purposes. Any appreciable potential due to the glass itself, variously known as the self, strain, or asymmetry potential, must be determined, however, and a corresponding correction applied to the over-all potential. The asymmetry potential is readily measured with the ordinary glass electrode by having the same kind of solution and auxiliary electrode on each side. (With the metal-connected glass electrode it is not possible to determine the asymmetry potential, which is included in the calibration.) With good electrodes, this potential is seldom more than a few millivolts at the start and tends to decrease to zero in a short time. It is less confusing to omit such a term from the above equations, with the understanding that it must be subtracted (algebraically) from E when necessary, as will be illustrated below.

The equations are given in algebraic form, and potential values must be inserted with proper signs. In general, the sign of any electrode is defined as that of the charge on the outside metal terminal. As the saturated calomel electrode is used here as the standard half cell for reference, the sign of the measured cell potential (E) is that of the other electrode with respect to the calomel, or the same as that on the outside terminal of the other electrode. A little consideration of the circuit conditions also shows that the sign of a glass bulb or membrane electrode is that of the inside connecting electrode (whether silver-silver chloride, calomel, etc.) in the solution the pH of which is kept constant. This is brought out in Figure 4, in which the relative number of + or − signs indicates conventionally the tendency for current to flow to the external circuit in the ordinary sense. With the metal-connected glass electrode, the sign is that of the terminal of the metal coating, wherever this is located; that is, whether or not the electrode contains, or is immersed in, the solution to be tested.

The following calculations are typical for a glass bulb or membrane electrode filled with 0.05 M acid potassium phthalate and mounted between two saturated calomel electrodes.

With 0.05 M acid potassium phthalate also placed on the outside—

$E_1 = -0.002$ volt = asymmetry potential (measured).
(Inner calomel negative to outer calomel. In other instances the sign might be opposite.)

With solution of unknown pH placed on the outside:

$E_2 = -0.126$ volt (measured).
(Inner calomel negative to outer calomel.)

$E = E_2 - E_1 = -0.126 - (-0.002) = -0.124$ volt.

$$\text{pH} = 3.97 - \frac{-0.124}{0.0591} = 3.97 + 2.10 = 6.07$$

As most publications on this subject omit any explanation of the signs, it is believed that the above brief treatment may be helpful.

The conventional straight line graphs for the various equations listed in Table 2 are shown for illustrative purposes in Figure 5. Such a diagram is useful for bringing out the relations involved and for quickly plotting the position of an ordinary glass electrode when the conditions are changed. The following relations should be noted:

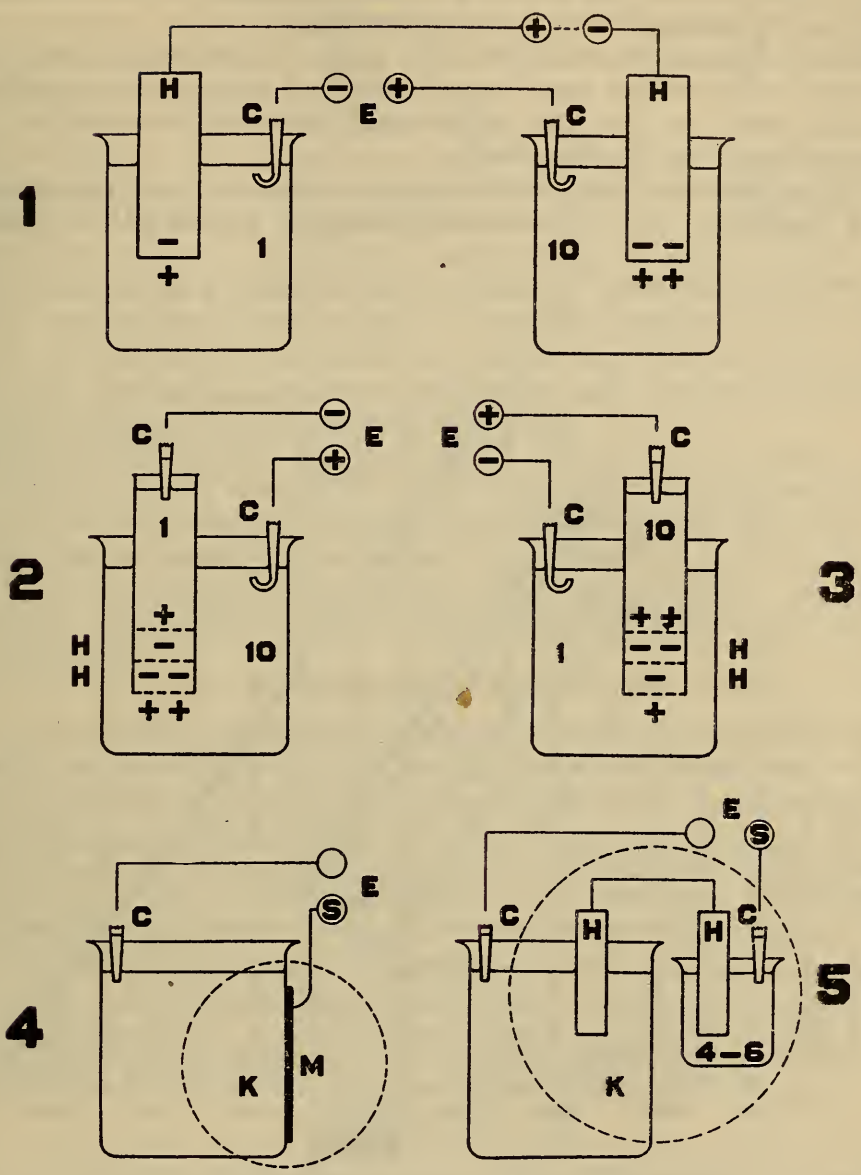

FIGURE 4.—*Sign of electrodes*

(Only the tips of calomel electrodes are shown). *1*, example of two hydrogen electrodes connected with two calomel electrodes. *H*=hydrogen electrode. *C*=calomel electrode. pH of left solution=1. pH of right solution=10. *E*=measured potential. The hydrogen electrode in the solution of lower pH is + to the other hydrogen electrode. The calomel electrode in the solution of higher pH is + to the other calomel electrode. Taking one calomel electrode as the standard of reference, in a solution of fixed pH, the sign of *E* is that of this electrode; *2*, example of a membrane glass electrode filled with a solution of relatively low and constant pH. The membrane is imagined to be divided into two hydrogen electrodes connected in series as in (*1*). *H*, *C*, and *E* as before. pH of solution within membrane electrode=1. pH of solution in beaker=10. The calomel electrode within the glass electrode is the standard of reference and is negative, which is taken as the sign of *E*. This results from the lower hydrogen electrode being negative to the upper hydrogen electrode, just as in (*1*) the right hydrogen electrode is negative to the left hydrogen electrode. The relation is similar if a silver-silver chloride electrode is substituted for the inside calomel electrode; *3*, this is like (*2*), with all conditions reversed. As before, the sign of *E* is that on the inside calomel electrode, or + in this case; *4*, example of a containing type metal-connected glass electrode. pH of the solution to be measured=*K*. The sign of *E* is that on the terminal *S*, which is connected to the metal, as is explained in (*5*); *5*, the area within the dotted circle represents in more detail the supposed conditions within the dotted circle of (*4*). The glass-metal section can be substituted by two hydrogen electrodes in series, as in (*1*). One hydrogen electrode is immersed in the solution of pH=*K* and the other hydrogen electrode is immersed in a solution of constant pH, in these experiments somewhere between 4 and 6. The circuit is completed by another calomel electrode in the latter solution. This electrode becomes the standard of reference, as in (*1*). The sign of *E* is that on terminal *S* as in (*4*)

(*a*) All lines are parallel and have the same (negative) slope of 0.05912 volt per unit pH at 25° C., corresponding to the denominator of the last right-hand term of the equations.

(*b*) Each line intersects the zero axis of abscissae (that is, each electrode reads zero to a saturated calomel reference electrode) at a pH value equal to the first right-hand term of its equation, or the "pH constant" for the electrode.

(*c*) When the electrode mounting or connection is symmetrical like that of Kerridge, the pH constant is equal to the pH of the inside

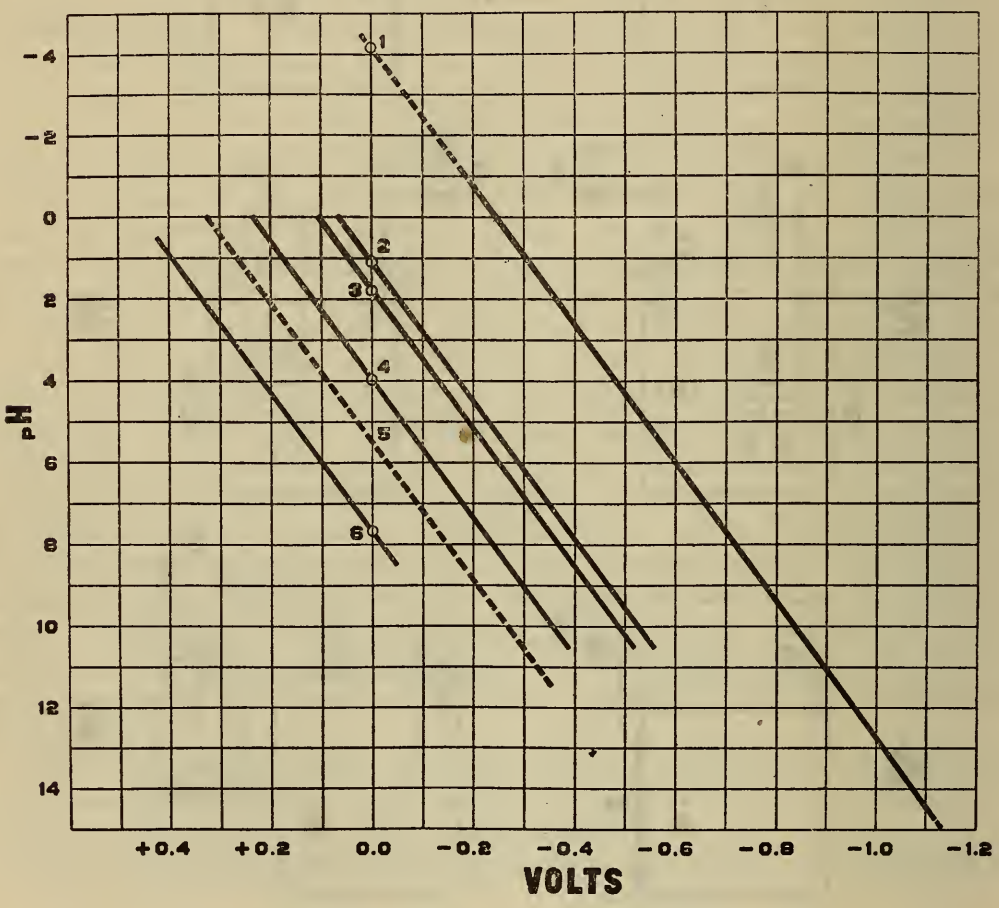

FIGURE 5.—*Standard graphs of electrode equations*

pH and potential in volts v. saturated calomel electrode at 25° C. (See Table 2.) *1*, Hydrogen electrode; *2*, glass electrode filled with 0.1 *N* HCl and connected with an inside saturated calomel electrode; *3*, glass electrode filled with 0.1 *N* HCl and connected with an inside silver-silver chloride electrode; *4*, glass electrode filled with 0.05 *M* acid potassium phthalate and connected with an inside saturated calomel electrode; *5*, metal-connected glass electrode. This line is shown dotted to indicate that the position is only approximate and must be determined by calibration; *6*, quinhydrone electrode

solution. Hence, a line can be immediately drawn in for a given value of pH for the inside buffer solution.

(*d*) The sign of the electrode reverses when the pH of the solution being measured passes the electrode constant, being positive for lower pH values and vice versa.

(*e*) An electrode (glass or other) will be positive to any other electrode placed in the same solution, if the first electrode line lies to the left, and vice versa.

(*f*) The approximate useful pH range for each electrode is indicated by the positions of the ends of its line.

The various kinds of standard and glass electrodes used in this investigation were calibrated or checked by means of a series of buffer solutions that were either 0.05 or 0.1 *M* and prepared according to the directions of Clark (24). These solutions included phthalate, phosphate, borate, and carbonate and were standardized by either the hydrogen or quinhydrone electrode.

The suitability of an electrode for measuring hydrogen ion concentration depends upon the extent to which the accuracy and reproducibility are affected by various factors. Among these are: (*a*) Useful pH range; (*b*) age; that is, any change in the calibration with time; (*c*) alkali salts (salt error); (*d*) heavy metal salts; (*e*) proteins; and (*f*) oxidants and reductants. Certain "poisons" may also be found in some of these categories. Thus, copper sulphate (a heavy metal salt) poisons a hydrogen electrode and sodium bisulphite (a reductant) poisons a quinhydrone electrode.

A brief study was accordingly made to determine the effects of the above factors on the operation of the metal-connected glass electrode. It should be emphasized that these experiments were not designed to redetermine the constants of certain solutions, nor to establish exact limits for the electrode, but merely to determine trends. In this way, the general behavior could be defined and possible means of improvement indicated.

2. USEFUL pH RANGE

Every secondary electrode is subject to errors outside of some favorable range of pH, which therefore needs to be defined. Briefly, within the limits of accuracy (±0.1 pH) of these measurements the metal-connected glass electrodes were found to function linearly [7] and reproducibly between pH–1 and pH–11, in dilute buffer solutions. Down to pH–0; that is in concentrated acid solutions, fairly satisfactory readings could be obtained by frequent calibration. Above pH–11, hydroxide solutions of increasing concentration must be used and attack of the glass surface is probable. Readings above pH–11.5 were unsatisfactory. In general, any kind of electrode tends to show discrepancies in the strongly acid and alkaline ranges.

3. EFFECT OF AGE

The metal-connected electrodes were calibrated occasionally by means of buffer solutions, using the technique previously described. Typical calibrations are shown for illustrative purposes in Figure 6 [7]. The approximate variation in the constant thus determined for the same electrodes over a period of about eight months [8] is shown in Figure 7.

The change in the constant is evidently due to a change in the initial potential of (or in) the glass. This is usually accompanied by a slight increase in resistance (Table 1), but without any apparent decrease in accuracy. The change can not, therefore, be definitely ascribed either to increased surface leakage or to deterioration of the

[7] MacInnes and Dole (31) and MacInnes and Belcher (34) showed by very accurate measurements that glass of the type used for electrodes did not function linearly in very alkaline (31) (34) or very acid (34) solutions, especially when these were concentrated. In dilute solutions, however, the deviation was less than ±0.1 pH for the pH range used in the present work. This point should be kept in mind, however, whenever work of higher accuracy is attempted with metal-connected glass electrodes.

[8] A recent examination of one of these electrodes (No. 2) showed it to be in useful condition at the end of one year. The constant was then about 5.83, which indicated practically no change in the last four months.

glass. Except in rare cases, the normal drift or rate of change was probably less than 0.01 pH per day. In two cases the constant decreased, and at an increasing rate (fig. 7, Nos. 1 and 3), while in the third case (fig. 7, No. 2) it is remarkable that very little change occurred, although this electrode was most frequently used in the experiments.

The electrodes were actually used to a much greater extent than is indicated in Figure 7, but were not always calibrated for other than a required short range of pH, which did not necessarily include the pH constant. Figure 7 merely records observed limits and was not used for purposes of measurement. Like other types of electrodes,

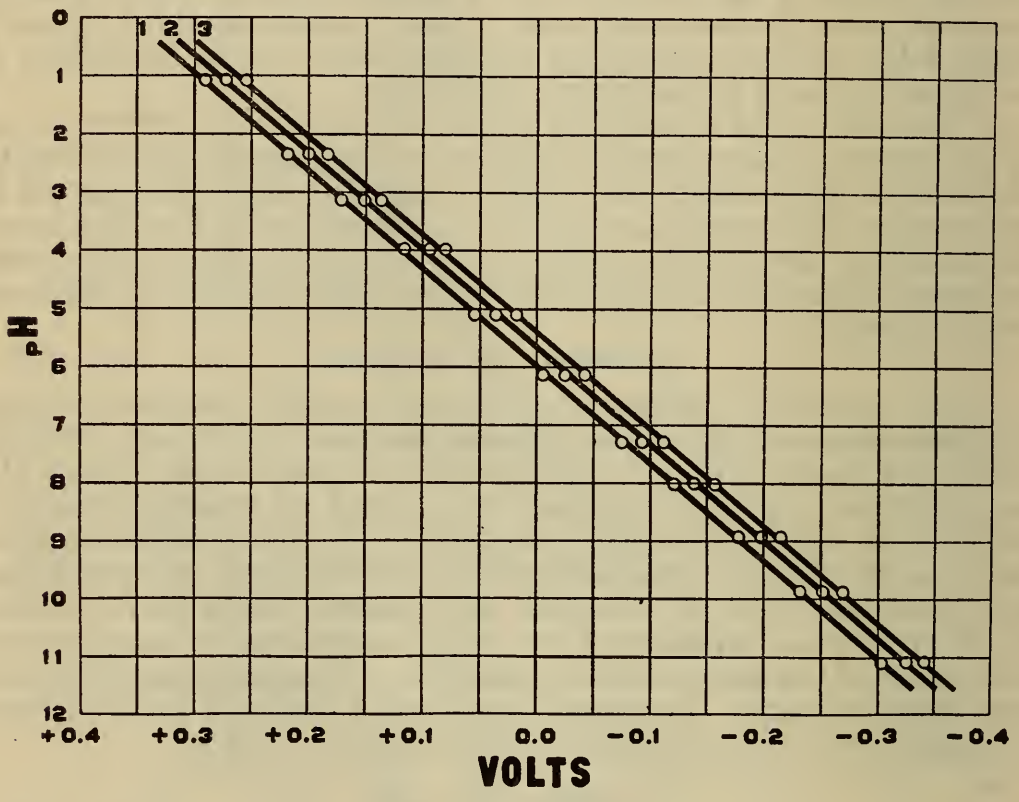

FIGURE 6.—*Actual calibrations of three m etal-connected glass electrodes of the containing type*

pH and potential in volts versus saturated calomel electrode at 25° C.

the metal-connected glass electrode required frequent checking, depending on the accuracy desired and the kind of solution under study. It was found advantageous to check an electrode in use several times daily.

4. EFFECT OF ALKALI SALTS (SALT ERROR)

At a given pH, the total concentration and kind of neutral salt present affect the potential of an electrode, causing what is known as the salt error. For the hydrogen electrode this error is zero by definition and for the quinhydrone electrode it is relatively small. To determine the approximate salt error for the metal-connected glass electrode, buffer solutions were prepared containing a large amount of potassium chloride or sodium chloride. The apparent change in pH was then determined.

The results obtained are shown in Tables 3 and 4.

TABLE 3.—*Effect of addition of normal potassium chloride to buffer solutions*

Buffer solution		Change in pH after addition			Salt error	
Composition	pH without addition	Hydrogen electrode	Quinhydrone electrode	Metal-connected glass electrode	Quinhydrone electrode	Metal-connected glass electrode
0.1 *N* HCl	1.10	−0.20	−0.18	−0.24	+0.02	−0.04
0.05 *M* $KH_2PO_4+K_2HPO_4$	7.00	−.41	−.37	−.44	+.04	−.03
0.1 *N* K_2CO_3	11.20	−.28	----------	−.32	----------	−.04

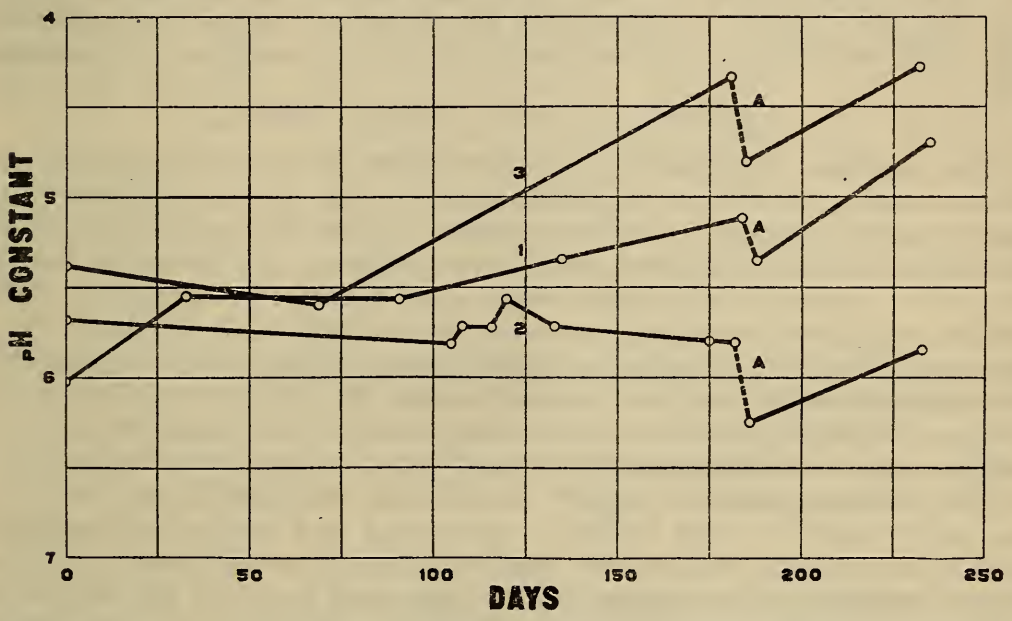

FIGURE 7.—*Variation of pH constant with time for three metal-connected glass electrodes of the containing type*

pH and potential in volts versus saturated calomel electrode at 25° C. *A*, Effect of applying 1,000 volts d. c. for a measurement of resistance

TABLE 4.—*Effect of addition of sodium chloride to buffer solutions*

Buffer solution composition.	NaCl added *N*	Change in pH after addition			Salt error	
		Hydrogen electrode	Quinhydrone electrode	Metal-connected glass electrode	Quinhydrone electrode	Metal-connected glass electrode
0.1 *N* HCl	1	−0.26	−0.28	−0.24	−0.02	+0.02
	2	−.50	−.43	−.41	+.07	+.09
	4	−.90	−.79	−.66	+.11	+.24
0.05 *M* $KH_2PO_4+K_2HPO_4$	1	−.71	−.62	−.70	+.09	+.01
0.1 *N* K_2CO_3	1	−.46	----------	−.76	----------	−.30
	2	−.66	----------	−1.03	----------	−.34
	4	−.81	----------	−1.39	----------	−.58

The addition of salts caused a decrease in pH (an increase in hydrogen ion activity) in every case. As mentioned above, the change for the hydrogen electrode is attributed to an actual change in the solution and the differential change between the hydrogen and any other electrode then becomes the salt error for that electrode.

Table 3 shows that the salt error caused by potassium chloride up to 1 *N* is only a few hundredths pH throughout the useful range of the

metal-connected glass electrode, or about the same as for the quinhydrone electrode. The salt error caused by sodium chloride (Table 4) is also low in the acid and neutral ranges, but is quite appreciable in the alkaline range.

While these data are not complete, it seems safe to conclude that for best results the total salt concentration should be kept below 1 *N* if possible, and that potassium salts are preferable in alkaline solutions. When high salt concentrations are unavoidable it may be possible to secure more accurate measurements by calibrating the electrode in concentrated buffer solutions.

Similar results have been reported by Hughes (23), Kahler and De Eds (38) and others. Various investigators have noted that divalent ions, such as calcium, have a smaller effect than sodium or potassium ions.

5. EFFECT OF HEAVY METAL SALTS

The presence of a heavy metal salt often makes electrometric pH determinations difficult. Specific applications of an inappropriate nature are, of course, readily excluded. These include cases where the reagent used precipitates metal from solution, as gaseous hydrogen does with copper and quinhydrone with silver. In addition, difficulties may arise from the presence of impurities, such as colloids (2), from oxidation-reduction potentials including those possibly caused by reduction of metal ions to subvalent states (3) (4) (26), side reactions (18), and adsorption effects. It must also be remembered that these solutions are unbuffered unless a solid phase of hydroxide is present.

The measurements on heavy metal salt solutions were made to compare results by the different electrodes and not to redetermine hydrolysis points. Only the nickel ammonium sulphate and the copper sulphate were recrystallized salts and none of the solutions was treated with the corresponding metal hydroxide. The salts used were, however, all of high quality and there is reason to believe that the values obtained are typical, except possibly for manganese.

Colorimetric measurements of pH (uncorrected) could be obtained conveniently with these solutions and were therefore made by the Gillespie drop ratio method (24).

The results obtained with a few typical heavy metal solutions are given in Table 5.

TABLE 5.—*Effect of heavy metal salts on electrodes*

Solution 0.05 *M*	pH of solutions				
	Hydrogen electrode	Quinhydrone electrode	Membrane glass electrode	Metal-connected glass electrode	Colorimetric (uncorrected) [1]
$ZnSO_4$	5.2—5.6	5.1—5.8	6.15	5.80	6.55 B. c. p. 6.55 B. t. b.
$MnCl_2$	5.5—5.6	4.8—5.2	6.05	5.95	6.80 B. c. p. 7.00 B. t. b.
$NiSO_4$ [2]	5.20	5.40	5.45	5.40	5.70 M. r. 5.80 B. c. p.
$CuSO_4$		4.20	4.40	4.30	4.75 B. p. b. 4.50 M. r.
$HgCl_2$			3.60	3.50	3.80 B. p. b.
$AgNO_3$ [3]				5.07	6.65 B. c. p. 6.80 B. t. b.

[1] B. p. b., brom phenol blue; M. r., methyl red; B. c. p., brom cresol purple; B. t. b., brom thymol blue.
[2] As $NiSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$.
[3] 0.1 *M*.

The two types of the glass electrode showed good agreement in all the solutions except that of zinc sulphate. In this case the metal-connected electrode gave a value that was nearer than that of the membrane electrode to the hydrogen and quinhydrone values, although these were unsteady. Britton's (14, p. 2120) result for a more dilute (0.025 *M*) solution was 5.2 by the hydrogen electrode. Kolthoff and Kameda (42) found for 0.1 *M* solution a value of 5.67 by means of a specially prepared hydrogen electrode (with a bright platinum deposit) and colorimetrically by methyl red a value of 5.66, practically the same. Britton and Dodd (45) have recently found about 6.3 (interpolated from their fig. 1, p. 1943) for a 0.01 *M* solution, by the glass electrode. Britton and Robinson (46) have discussed the status of this subject. Some previous investigators (2) (21) (22) (26) have also reported a drift of the hydrogen electrode in zinc solutions.

The two types of the glass electrode agreed closely with the quinhydrone electrode in the nickel ammonium sulphate solution. Such solutions have, of course, a somewhat lower pH than do those of nickel sulphate. Better agreement between the quinhydrone and hydrogen electrodes is usually obtained in nickel solutions, particularly at higher concentrations or when buffered (30).

In the copper sulphate solution the glass electrodes also showed good agreement with the quinhydrone. Values for 0.05 *M* $CuSO_4$ at 18° C have been reported by O'Sullivan (17) using the quinhydrone and by Hughes (23) using the glass electrode, as 4.14 and 4.24, respectively, which are in good agreement with the present results. Britton's (14, p. 2148) value for 0.02 *M* copper sulphate was 5.4 by the oxygen electrode.

In the manganese solution readings were somewhat unsteady with all electrodes used. Those made with the glass electrode were considerably higher than those with the hydrogen or quinhydrone. The latter both showed drifts and did not agree closely. Rideal (18) has pointed out that manganese salts tend to catalyze the auto-oxidation of quinhydrone, so that the result by the quinhydrone electrode is doubtful. The accepted value for manganese solutions in the literature is 8.5 to 8.8 (11) (14, p. 2110) by the hydrogen electrode, indicating that these solutions at equilibrium conditions are slightly alkaline, a conclusion that seems anomalous in view of the weakly basic character of divalent manganese. Possibly an oxidation-reduction potential interferes.

The value obtained for the mercuric chloride solution is close to that of Britton and Dodd (45), who found about 3.7 (interpolated from their fig. 1, p. 1943) for a 0.01 *M* solution, by the glass electrode. This replaces an earlier and much higher value of 7.3, by the oxygen electrode, reported by Britton (14, p. 2148).

The value for the silver nitrate solution agrees with that of about 5.0 (interpolated from their fig. 1, p. 1943) found for a more dilute (0.01 *M*) solution by Britton and Dodd (45), by the glass electrode. Britton (14, p. 2148) previously found 5.7 for 0.02 *M* silver nitrate, by the oxygen electrode. He then adopted "pH 9 (?)" tentatively, however, basing this figure on calculations of the solubility product of silver hydroxide. Evidently, this value was too high and the experimental one was nearer correct. Further data and discussion have been given by Britton and Robinson (46). Horovitz (10, p. 389) thought that he detected a silver electrode function of glass in silver

solutions, but this was not confirmed by Hughes (23). Any direct effect of the silver (or copper) coating of the metal-connected electrode is unlikely, as the glass used contained no heavy metals and was comparatively thick.

In general, the results by the colorimetric method (uncorrected) show somewhat higher salt errors for the indicators than would be expected for such dilute solutions. Combination between metal ion and indicator may have occurred in some cases.

6. EFFECT OF PROTEIN

It is well known that proteins are likely to disturb electrode readings. Gelatin was selected for trial, as it is a substance of special interest in electrochemical work, and a few experiments were made on solutions containing various amounts at low, intermediate and high pH values. The data obtained are presented in Table 6.

TABLE 6.—*Effect of gelatin*

Buffer solution	Gelatin g/l	pH		
		Hydrogen electrode	Quinhydrone electrode	Metal-connected glass electrode
0.1 *N* HCl	0	----------	1.13	1.19
	1	----------	1.19	1.17
	5	----------	1.19	1.17
	10	----------	1.17	1.14
0.05 *M* $KH_2PO_4+K_2HPO_4$	0	----------	6.98	7.01
	1	----------	6.99	7.01
	5	----------	6.98	7.02
	10	----------	6.96	6.98
0.1 *N* K_2CO_3	0	11.00	----------	11.03
	1	10.94	----------	10.90
	5	10.77	----------	10.88
	10	10.59	----------	10.73

Large amounts of gelatin did not appreciably affect the readings of the metal-connected glass electrode at low and intermediate pH values, as compared with the quinhydrone electrode. It is well known that the quinhydrone electrode is itself affected by some proteins. The metal-connected electrode agreed closely with the hydrogen electrode at the high pH when only small amounts of gelatin were present. The pH of the carbonate solution actually decreased when gelatin was dissolved in it. This was accompanied by a slight precipitation.

7. EFFECT OF OXIDANTS AND REDUCTANTS

Strongly oxidizing or reducing compounds cause a potential separate from that of hydrogen ions and usually great enough to prevent the use of the hydrogen or quinhydrone electrode. The latter can be used occasionally, for instance, in dilute nitric acid. Sometimes a metal-metal oxide electrode can be substituted, as that of mercury, manganese, or antimony, which may be convenient even if empirical. Indicators are usually unsatisfactory.

Previous types of the glass electrode have been shown by Hughes (9) MacInnes and Dole (27) and others to be quite unaffected by oxidation-reduction potentials. To determine if this relation holds also for the metal-connected electrode, comparative measurements with this and the membrane glass electrode were made on a few typical solutions. The results are presented in Table 7.

TABLE 7.—*Effect of oxidants and reductants*

Solution	pH		Solution	pH	
	Membrane electrode	Metal-connected electrode		Membrane electrode	Metal-connected electrode
0.1 *M* HNO_3[1]	1.10	1.20	0.1 *M* $K_2Cr_2O_7$	3.75	3.85
1 *M* CrO_3	.45	.65	0.2 *M* K_2CrO_4	9.25	9.30
0.45 *M* $K_2Cr_2O_7$[2]	3.60	3.80	0.05 *M* As_2O_3	5.60	5.55
1 *M* K_2CrO_4	9.45	9.55	0.25 *M* $Na_2S_2O_5$	4.90	4.80
0.2 *M* CrO_3	.90	1.05	0.1 *M* NaCN[3]		11.0

[1] 1.14 by quinhydrone electrode.
[2] Saturated solution.
[3] 11.5 (maximum) by hydrogen electrode.

The two types of glass electrodes gave about the same results. The lower values by the membrane electrode, particularly in the more concentrated oxidizing solutions, are probably more accurate, as this type seems less subject to disturbances, possibly of the nature of adsorption effects.

The results for the chromic acid and chromate solutions agree roughly with the end points of the titration curves published by Hughes (9) and by Britton (12) (13) (43, p. 73, p. 162). Hughes used a glass electrode of the bulb type and 0.1 *M* chromic acid, while Britton used both oxygen and hydrogen electrodes in very dilute (about 0.025 *M*) chromic acid.

It is of interest to note the great difference in strength between dichromic and chromic acid, on account of which chromate solutions are distinctly alkaline because of hydrolysis. (The acidity of the dichromate solutions may be attributed to secondary dissociation of the dichromate ion.)

Readings in the bisulphite solution were often unsteady, probably because of absorption of oxygen from the air and a resulting change in acidity. The hydrogen (43, p. 73), quinhydrone and oxygen (43, p. 73) electrodes all fail in bisulphite or sulphite solutions.

The value for sodium cyanide is consistent with the hydrolysis measurements of Harman and Worley (16) and with a measurement by Britton and Robinson (40) on dilute potassium cyanide solution (0.04 *M*), with the antimony electrode. Britton and Dodd (45) later found the glass electrode to be more accurate than the antimony electrode, in cyanide solutions. The hydrolysis of alkali cyanide is evidently about the same as that of alkali carbonate.

8. APPLICATIONS

Applications of the metal-connected glass electrode in research have been made by the author in connection with pH measurements

on chromic acid and chromium chromate solutions, cyanide silver-plating solutions (preferably diluted), and ammoniacal silver bromide-gelatin photographic emulsions. In general, consistent and useful results were obtained. These will be published in separate papers by other investigators.

V. SUMMARY

1. Glass electrodes with a direct metallic connection may be constructed having comparatively good accuracy and sensitivity.

2. This shows that an equilibrium between hydrogen ions on opposite sides of a glass wall is not essential to the functioning of glass as an electrode, and suggests that deep penetration of hydrogen ions into the glass may not occur.

3. The metal-connected electrodes may be constructed with walls thick enough to make breakage unlikely with ordinary care in handling.

4. Their useful life is indefinite and measured by months or years.

5. Only small errors are caused by alkali salts in moderate concentration, by heavy metal salts in low concentration and by gelatin.

6. Oxidation-reduction potentials have little, if any, effect with this or other types of glass electrodes.

VI. ACKNOWLEDGMENTS

The writer acquired his first experience with the technique of glass electrodes during March and April, 1929, as a guest at the Rockefeller Institute for Medical Research in New York City. Grateful acknowledgment is herewith made to Dr. D. A. MacInnes of that institution and to Dr. M. Dole, formerly there but now at Northwestern University, Evanston, Ill.

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145879—32——10